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**Wright State University:  
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Dayton OH 45435

**Final Report**

to

**Office of Naval Research**

Attn: Dr. Yoon Soo Park  
ONR: Code 312  
Ballston Tower One, 800 North Quincy Street  
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**Title: International Workshop on ZnO**

**Grant N00014-99-1-1054**

**Date of report: 12Dec01**

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The First International Workshop on ZnO was held at the Holiday Inn 1675 in Dayton, Ohio, on October 7-8, 1999. David Look (WSU) served as the chairman, and was assisted by Cole Litton (AFRL/MLPA), Mike Alexander (AFRL/SNHX), Hadis Morkoc (Virginia Commonwealth University), and Yoon Soo Park (ONR). Financial support was received from ONR and AFOSR, and other sponsors included The Air Force Research Laboratory and Wright State University. Because this was the first meeting ever devoted solely to ZnO (as far as we know), a large amount of extra work was required in compiling a mailing list; in this regard, Delayne Scales (AFRL/MLPA) was very helpful. Also, there were the usual time-consuming chores of establishing a budget, communicating with prospective attendees, obtaining funding, and selecting a program, mostly carried out by Dr. Look. In the end, the workshop was very successful, with more than seventy scientists and engineers, from ten different countries, participating. The program included thirty-six contributions, ranging from first-principles theory to practical device applications. For example, a lively debate developed on the ordering of the valence bands, and, on the more practical side, a very good MSM uv detector was presented. A strong interaction between basic and applied researchers is necessary for rapid progress in any field.

The key limitations to real progress in the areas of ZnO photonic and electronic devices are p-type doping and a good Schottky barrier; both of these topics were addressed at the workshop, and significant progress was reported. Bulk crystal growth is proceeding well on all fronts (vapor-phase, hydrothermal, and melt), and Eagle-Picher Technologies is now offering 40-mm vapor-phase wafers for sale. Similarly, several types of epitaxial growth (PLD, MOCVD, and MBE) have been successfully exploited, and quantum wells and superlattices have been fabricated from the ZnO, MgZnO, CdZnO family. The future of ZnO commercialization depends, in part, on how well it compares with its chief competitor, GaN. In this regard, it was pointed out that ZnO has (1) a higher exciton binding energy; (2) a higher velocity at high fields; (3) a native substrate; and (4) better radiation hardness.

Representatives of Air Force and Navy funding agencies were present at the workshop, and it is hoped that a critical mass of research can be engendered in the US. If not, the field will have to be conceded to Japan, in which some very impressive work is already taking place, and possibly Europe, within which a ZnO consortium is going to be formed as a result of interactions at the workshop. Our WSU/AFRL group has demonstrated the first optical laser and the extent of radiation hardness, and the US definitely leads in the fundamental understanding of the material; however, the rest of the world, especially Japan, leads in several other aspects, and is proceeding rapidly. Now is the time for the US and, in particular, the DoD (because of space applications) to make a commitment to the development of ZnO photonic and electronic devices.

# **International Workshop on Zinc Oxide**

**Dayton, Ohio  
October 7-8, 1999**

**20020125 194**

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## Evolution of ZnO

**Yoon-Soo Park**  
**Office of Naval Research**  
**800 N. Quincy Street**  
**Arlington, VA 22217**

ZnO has attractive electronic, mechanical and thermal properties with many applications. Its bandgap, just in the soft UV, makes it the most favored material for suntan lotions with very effective UV blocking capabilities. Its attractive thermal conductivity opened up applications in automobile tires for heat removal. Among the most attractive properties of ZnO as a semiconductor are its bandgap, large exciton binding energy, and a very efficient radiative recombination process. The bandgap of ZnO can be increased and decreased with addition of Mg, possibly Be as well, and Cd, respectively, which paves the way for heterojunctions. Consequently, carriers can be confined and light can be guided, essential gradients for laser operation. In fact lasing action through optical pumping has been observed. Unlike GaN, high quality substrates can be and has been produced by a variety of techniques. As is the case for any large bandgap ionic crystal, it is difficult to obtain p-type conductivity in ZnO as well. Recently, however, p-type conductivity has been reported which means that all the elements needed for semiconductor lasers are available. Momentum for the recent surge of interest in ZnO is in part attributable to the fact that ZnO and GaN share the same lattice structure with very similar lattice parameters which means that ZnO may be a good substrate for GaN epitaxy.

In this presentation, evolution and recent developments in ZnO and related structures will be discussed.

## ZINC OXIDE (ZnO) SUBSTRATES

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Single crystal zinc oxide (ZnO) is a potentially valuable material for many light emitter, detector, and power device applications. The tendency for the material to decompose at high temperature has precluded the crystallization from the melt. In this work, a high-pressure, induction-melting technique was used to melt zinc oxide. The high-pressure process prevents the decomposition of the zinc oxide, while a proprietary melt containment technique serves to contain the ~1975°C melt without introducing impurities. The ability to obtain a pool of molten ZnO enables large diameter ZnO to be crystallized using conventional melt growth processes. Centimeter-sized crystals were obtained in the preliminary experiments by crystallizing in a Bridgman-type arrangement. Optical and structural analysis of these crystals included x-ray diffraction, photoluminescence spectroscopy, and electron microscopy. Temperature dependent Hall data was measured for representative crystals. Ultimately, this technology will provide low cost ZnO substrates for the fabrication of ZnO-based devices, as well as nitride devices.

Conference Name: First International Workshop on ZnO

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Oral Presentation Preferred

Key Terms: oxides, II-VI bulk, lasers, substrates, wide band gap

## High Quality Hydrothermal ZnO Crystals

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### ABSTRACT

Zinc Oxide crystals have historically been grown in hydrothermal autoclaves with a basic mineralizer; however, doubts have been raised about the quality of such crystals because they have often exhibited large x-ray rocking curve widths and low photoluminescence (PL) yield with large linewidths. Several ZnO crystals were grown hydrothermally and sliced parallel to the c-plane. This resulted in opposite surfaces (the  $C^+$  and  $C^-$ ) exhibiting pronounced chemical and mechanical differences. Different surface treatments were investigated and compared by PL both at room temperature and liquid helium temperatures, and by double axis X-ray rocking curve measurements. The high quality of hydrothermally-grown ZnO is substantiated by the narrow rocking curve widths and sharp PL peaks obtained. A critical factor in obtaining these results was found to be surface preparation.



"Properties of Vapor Grown ZnO"

G Cantwell (1), J.L. Boone (2), J.E. Thomas (3), D. Eason (1)

(1) Eagle-Picher

(2) University of Missouri-Rolla

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Growth methods typically used for II-VI compounds, physical vapor transport and melt growth, are difficult to use with ZnO due to its high melting point and high temperature stability. Here, we will describe the properties of the bulk single crystals of ZnO grown by the chemical vapor transport method using hydrogen as the transporting agent. These crystals are being grown at 2- and 3-inch diameter with high crystalline quality at temperatures less than 1200 C. Measurements of crystalline and optical quality will be presented. Additionally, a model has been developed to describe the transport and crystal growth process. A comparison of the experimental and theoretical results will be presented.

## ZnO bulk and thin layer vapor growth

R. Triboulet, J.-M. Ntep, A. Lusson, V. Sallet, J.F. Rommeluère, G. Didier, D. Ballutaud, S. Said Hassani, A. Tromson-Carli  
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ZnO is an attractive substrate for the growth of epilayers of GaN with which it shows the same crystallographic structure with a lattice mismatch less than 1.8%. Furthermore ZnO, with an exciton binding energy (60 meV) well above the thermal energy at room temperature, has been shown to display excitonic stimulated emission up to 550 K, the highest temperature yet reported for any semiconductor<sup>1</sup>.

Residual water present in gases or gaseous mixtures such as H<sub>2</sub>, Ar or H<sub>2</sub> + H<sub>2</sub>O is shown to act as sublimation activator of the vapor phase transport of ZnO. The thermodynamics constants of the water activated sublimation - energies of activation, sublimation and condensation and enthalpy of formation - are determined through close spacing vapor transport experiments from a fit to the variation of the growth rate as a function of the substrate temperature, using a theoretical model. The ZnO sublimation mechanism is shown to be complex, by comparison with the simple ZnSe one, involving a competition between two different mechanisms : one associated with ZnO, the other one with Zn.

As an alternative, chemical vapor transport using chlorine as the transporting agent is studied for the growth of ZnO crystals. A chemically assisted sublimation process, like in the case of water, is suggested, chlorine acting as a sublimation activator. 1 cm<sup>3</sup> size crystals are obtained after 40 days using a source temperature of 1000°C and a source temperature-growth temperature difference  $\Delta T$  of ~30°C. Rocking-curve FWHM in the 30 arcsec range are measured and well resolved pseudo Kikuchi lines are observed on (0001) planes by electron scanning microscopy. The residual concentration of chlorine atoms in the crystals is estimated from XPS measurements to be about 0.05%. The electron concentration of the crystals at room temperature reaches values as high as  $3 \times 10^{19} \text{ cm}^{-3}$ . Assuming chlorine to be the residual donor, the ionization energy of chlorine in ZnO is found to be close to 23 meV.

ZnO layers are grown by MOCVD at atmospheric pressure using butanol and diethylzinc, respectively as oxygen and zinc precursors, introduced separately into the reactor. Polycrystalline layers deposited on (100) GaP and ZnSe substrates show photoluminescence spectra in which the donor-bound exciton dominates. The presence of the free exciton emission testifies to the good quality of the layers. Electrical measurements show a high residual n doping ( $10^{19}$  to  $10^{20} \text{ at/cm}^3$ ) likely due to oxygen vacancies rather than to residual impurities. The objective is now to decrease this high doping level in order to try to obtain p-type conductivity, never achieved in MOCVD.

<sup>1</sup>D.M. Bagall, Y.F. Chen, Z. Zhu, T. Yao, M.Y. Shen, T. Goto, Appl. Phys. Lett. 73 (1998) 1038.

# Crystal growth of isotopically pure ZnO by chemical vapor transport

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The possibility of growing crystals with controlled isotopic composition has opened a new field of solid state research, particularly in lattice dynamics [1]. Different isotope effects on the phonons and even on the electronic band-gap have been investigated in semiconductors (see ref. [2]).

For the extension of such studies to ZnO, we have combined the highly enriched isotopes  $^{64}\text{Zn}$  (99.4 %) and  $^{68}\text{Zn}$  (97.9 %) with the isotope  $^{18}\text{O}$  (99 %). In each case, and also for reference samples with natural isotopic composition ( $^{\text{nat}}\text{Zn}^{\text{nat}}\text{O}$ ), purification, synthesis, and crystal growth were performed in the same ampoule from small quantities of materials. The purification of Zn and its separation from natural oxide were achieved by sublimation of the Zn metal at temperatures of 350-450°C. This procedure led to a thin solid Zn layer which accelerated the synthesis of ZnO in an  $^{18}\text{O}_2$  atmosphere at temperatures above 500°C.

We have obtained wurtzite-type crystals of  $^{\text{nat}}\text{Zn}^{\text{nat}}\text{O}$ ,  $^{64}\text{Zn}^{18}\text{O}$ , and  $^{68}\text{Zn}^{18}\text{O}$  by chemical vapor transport at a source temperature of about 1000°C, using ammonium chloride as an agent. In an argon environment and under Zn excess, a limited number of these transparent yellowish, pyramid-like and prism-like crystals with lengths up to 2 mm appeared in the temperature range between 750°C and 950°C.

Raman scattering is being applied for the characterization of the samples and for the investigation of isotope effects on phonons.

- [1] M. Cardona, in: *Festkörperprobleme / Advances in Solid State Physics*, Vol. 34, ed. by R. Helbig, (Vieweg, Braunschweig / Wiesbaden 1994), p. 35.
- [2] A. Göbel, J. M. Zhang, T. Ruf, R. Lauck, and M. Cardona, *Phys.Rev. B* 59 (1999) 2749.

Hideyuki Maki

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Zinc Oxide (ZnO) is the wurtzite-type crystals with  $a_0=0.325\text{nm}$  and  $c_0=0.520\text{nm}$ . This structure can be described as planes composed of Zn and O ions stacked along the c-axis. Single crystals have well-defined polarity, and have two different surfaces, which are terminated by Zn and O ions on the (0001) and (000 $\bar{1}$ ) planes, respectively. This crystallographic structure causes physical and chemical properties of oppositely polarized surfaces remarkably different. In our previous paper, we evaluated the surface morphology of ZnO single crystals by atomic force microscope (AFM), and etching behavior of oppositely polarized surfaces was remarkably different. Although the topmost surface structure is important to understand the differences of the properties, there are little reports about the surface structure especially the surface relaxation on ZnO (0001) surface. In this paper, we analyzed the (0001) surface morphology of ZnO single crystals by an atomic force microscope (AFM) and their ionic configuration by CAICISS and reflection high-energy electron diffraction (RHEED). The single crystals were annealed at 950°C in oxygen gas flow. After annealing, the morphology of ZnO (0001) surface was observed in air at room temperature with AFM (Nanoscope III-a, Digital Instruments Ltd., USA) using a contact mode. The ionic configuration of the surface was analyzed by CAICISS (TALIS-9700, Shimadzu Corp., Japan) and RHEED (ULVAC Co. Ltd.) in UHV chamber. The apparatus consisted of an ion source and a time-of-flight (TOF) energy analyzer; the TOF analyzer was set at a coaxial position with the ion source. Just before CAICISS and RHEED observations, all the samples were heated in the analysis chamber at 900°C at a pressure of  $5 \times 10^{-7}\text{Pa}$  for 3 hours with the irradiation of oxygen radical to remove impurities adsorbed on the surface. An AFM image was measured for the surface annealed in O<sub>2</sub> gas. Although as-polished single crystal had rough surface, the surface changed to regular step/terrace structure after annealing. Step height for (0001) surface was about 0.25nm, corresponding to a half lattice parameter,  $c_0/2$ . As shown in RHEED pattern, the streaks of (1 $\bar{1}$ 0) structure were observed. The TOF spectra of CAICISS were measured for (0001) surface. Before annealing, the peak of Carbon ion was observed, although no O peak could not be seen. The peak of Zn was weak, while the broad peak of the multiple scattering was strong. As a result, the adsorptions such as Carbon Oxide were on the surface. After annealing, the peak of Zn ion and O peak was observed. In contrast, the peaks of C and multiple scattering decreased. The variation was caused by the cleanness of the surface. The polar angle dependence of Zn intensity of CAICISS was measured. From the results, the possibility of surface relaxation on ZnO (0001) surface was discussed.

A Thermodynamic Survey of Phase  
Formation and Stability of Transition Metal Thin Films on  
Single-Crystal ZnO

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Abstract:

Electronic devices capable of operation at elevated temperatures require an understanding of the chemical reactions which occur at the metal-semiconductor interface. Phases predicted from equilibrium thermodynamics are presented in the forms of both Ellingham and Gibbs ternary diagrams to understand the temperature sequence of oxide and metal-Zn compound formation and stability of the phases formed at the metal-ZnO interface. Of prime importance for stable metallizations is not only whether metal-Zn compounds exist but also if they are Zn rich. The existence of stable metal oxides generally encourages reactions of the metal with the ZnO substrate. Transition metals were deposited on single-crystal ZnO by electron-beam deposition or magnetron sputtering and annealed at temperatures approaching 1000 C. Resulting phases were identified by AES, XPS, and XRD and compared to the phases predicted by thermodynamic analysis. Limitations of the thermodynamic approach are also discussed.

"Assessment of Subsurface Damage in II-VI Semiconductors by Ion Channeling"

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The ultraprecision finishing of semiconductor materials continues to receive attention because of the critical need to provide surfaces with both extreme control of surface roughness and flatness as well as minimized damage of subsurface crystalline structure. Interest in assessing subsurface damage is motivated by the limitations which lattice disorder pose on device performance, and the fact that the extent of subsurface damage may provide a critical complement to surface finish in assessing machining/polishing performance. Here, we present results on the use of ion channeling to examine the extent and distribution of subsurface damage in ultraprecision machined and polished II-VI semiconductors. Single crystal (0001) oriented CdS was single point diamond turned over a range of depths of cut from 0.1-10 micrometers, and subsurface lattice disorder was examined for regions cut parallel to, and 30 degrees off, a preferred cleavage plane. The energy spectrum of 2 MeV  $He^+$  ions backscattered from the crystal surface was used to obtain depth profiles of lattice disorder. Results on lattice disorder produced by mechanically and chemo-mechanically polished CdS and ZnSe are also presented.

Submit to International Workshop on ZnO at the Holiday Inn I675 in Dayton, Ohio, on October 7,8, 1999

## Substrate Effects in Growth of Epitaxial ZnO Films

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### ABSTRACT

In this study, homoepitaxial and heteroepitaxial ZnO films have been investigated as a function of substrate pre-treatment and film deposition parameters. The films were synthesized by off-axis sputter deposition on (0001) ZnO and on (0001) sapphire substrates. The annealing temperature of (0001) sapphire was 1000 °C while the ZnO single crystal substrates were mechanically polished and annealed in air at different temperatures. The annealing temperature-dependence of ZnO substrates was studied to obtain a good growth surface for the homoepitaxial films. Films were grown at different temperatures and gas pressures employing mixed argon and oxygen gas. Several measurements were performed for these epitaxial films to study film morphology, structure, and electrical and optical properties using atomic force microscopy, x-ray diffraction, Hall effect measurements, and abortion spectroscopy. The films were found to have very smooth surfaces with a roughness  $\leq 5$  nm on a  $5 \mu\text{m} \times 5 \mu\text{m}$  area. The full width at half maximum (FWHM) of theta rocking curves of epitaxial films is  $\leq 0.3^\circ$ . The FWHM of the rocking curve of the best film is slightly larger than the single crystal substrate. Resistivity, Hall mobility, and carrier densities of these films strongly depend on the growth conditions, especially on the different gas pressures. The oxygen deficiency in films and ion bombardment during film growth may lead to the variation of electrical properties. A comparison of the results for homoepitaxial and heteroepitaxial ZnO films will be discussed in the presentation.

## Optoelectronic Applications of Sputtered ZnO Films

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### Abstract

Zinc oxide films can be grown, having a wide range of properties, by sputter deposition. By use of off-axis sputter deposition and in situ heating, we have been able to obtain extremely smooth ( $< 2\text{nm}$  rms roughness), nearly epitaxial (0001) ZnO films on (0001) sapphire substrates.<sup>1</sup> Most recently we have been able to obtain ZnO films with a (0002) rocking curve as low 250 arcsec. Such films can be semi-insulating or conducting depending on the growth and cooling conditions. We have also been able to deposit amorphous ZnO at ambient temperatures which can be subsequently transformed into highly oriented (0001) films by post-annealing. These films can also be tailored to be either highly resistive or conductive. Based on our IR transmission, Gwatt pulsed laser analysis, and resistivity measurements, ZnO appears to be a good material for a laser-hardened, infrared-transparent conductor. Its use in a variable optoelectronic grating will be discussed.

<sup>1</sup> "Ultra-Smooth ZnO Buffer Layers on (001) Sapphire," A.J. Drehman, S.-Q. Wang, and P.W. Yip, Proc. MRS. Nitride Semiconductors, 482, 289 (1998).



## Epitaxial Growth of ZnO Films on Si Substrates

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ZnO on Si offers an interesting opportunity that the various functional devices based on ZnO can be combined with the advanced Si electronics on the same substrate. ZnO films are also promising as a buffer layer in growing high quality epitaxial films of GaN and related alloys on Si substrates. Direct growth of epitaxial ZnO films on Si, however, is known to be a challenging task. It usually results in amorphous or polycrystalline films. The difficulty basically stems from the fact that Si surface gets easily oxidized during the nucleation stage of a ZnO growth process, forming an amorphous  $\text{SiO}_x$  layer.

In this work, we have investigated the use of a GaN buffer layer in growing epitaxial ZnO films on Si(111) substrates. We have used a rf magnetron sputtering technique in growing both GaN and ZnO films on Si substrates. First, a 300-500-nm -thick GaN film was grown as a buffer layer on the silicon substrate. X-ray diffraction analysis clearly confirmed that the GaN films grown on Si(111) are highly epitaxial. It has been reported that direct growth of GaN on Si(111) usually results in phase-mixed films and therefore a proper buffer layer (such as AlN or GaAs) has been used to obtain single-phase films. It should be mentioned that our GaN films, directly grown on Si, are of a single-phase monocrystalline hexagonal structure. ZnO films were then grown on top of the GaN buffer layer at a substrate temperature in the range of 550 - 750 °C. X-ray diffraction analysis shows that the ZnO films are of a monocrystalline hexagonal structure with an epitaxial relationship of  $\text{ZnO}[0001]//\text{GaN}[0001]//\text{Si}[111]$  along the growth direction and  $\text{ZnO}[11\bar{2}0]//\text{GaN}[11\bar{2}0]//\text{Si}[1\bar{1}0]$  along the in-plane direction. The GaN buffer offers unique advantages over other buffers reported so far (such as AlN and GaAs): good lattice match between GaN and ZnO (less than 2 % mismatch), and the controllability of electrical conductivity in a broad range, which will allow for more flexibility in device design. The successful growth of epitaxial ZnO/GaN heterostructures on Si demonstrates the feasibility and promise of integrating various functional devices on the same substrate.

## High quality epitaxial growth of ZnO, ZnMgO, and ZnO/GaN on sapphire for optoelectronics

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### ABSTRACT

ZnO is a direct band gap semiconductor with energy gap of 3.3 eV at room temperature (RT) and is being considered as a futuristic material for UV and blue light emitting devices. Recently, we have demonstrated high quality epitaxy of ZnO on sapphire and GaN/sapphire by pulsed laser deposition. Here we present our work in detail on the fabrication, processing, and characterization of device quality ZnO thin films. We will discuss the effects of the substrate temperature and the oxygen background pressure on the growth, epitaxy, point defect chemistry, and structural, optical, and electrical transport properties of the laser deposited epitaxial ZnO films. We show the possibility of obtaining desirable epitaxial quality and optoelectronic properties with smooth surface morphology of the ZnO films as a function of oxygen pressure during the initial and final stages of growth. The implications of these results with respect to the fabrication of superlattices and controlled n and p-type doping will be discussed.

Since the electrical and optical properties of these semiconductor heterostructures are governed by the nature of thin film growth, lattice misfit, defects, surfaces and interfaces, epitaxial growth of ZnO films on a lattice matched substrate is desirable. In this context, we have studied growth of ZnO on GaN (which is a low lattice mismatch (~2%) buffer layer) on sapphire. These films grown on epi-GaN/sapphire were found to be single crystalline due to the match of stacking order and a low lattice misfit between GaN and ZnO as compared to those grown directly on sapphire. Rutherford backscattering spectroscopy, ion channeling, and high resolution transmission electron microscopy studies revealed high-quality epitaxial growth of ZnO on GaN with an atomically sharp interface. X-ray diffraction and ion channeling measurements indicate near perfect alignment of the ZnO epilayers on GaN as compared to those grown directly on sapphire (0001). Low-temperature cathodoluminescence studies also indicate high optical quality of these films presumably due to the close lattice match and stacking order

between ZnO and GaN. Lattice-matched epitaxy and good luminescence properties of ZnO/GaN heterostructures are thus promising for UV lasers. Due to their lattice matching epitaxy, as well as thermal and optical compatibility, the ZnO/GaN heterostructures on sapphire may be useful for fabrication of hybrid optoelectronic devices exploiting advantages of both ZnO and GaN. We will also discuss on atomic long range ordering in the laser deposited ZnMgO films.

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## In-plane Acoustic and Optical Anisotropy in $(11\bar{2}0)$ ZnO Grown on $(01\bar{1}2)$ $\text{Al}_2\text{O}_3$

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$(11\bar{2}0)$  ZnO films grown on R-plane  $(01\bar{1}2)$  sapphire possess in-plane anisotropic properties which offer important device applications. We have grown ZnO films on R- $\text{Al}_2\text{O}_3$  by MOCVD at temperatures in the range of 350-500°C. The epitaxial relationship is determined to be  $(11\bar{2}0)$  ZnO// $(01\bar{1}2)$ , and  $[0001]$  ZnO //  $[0\bar{1}11]$   $\text{Al}_2\text{O}_3$  by x-ray  $\theta$ -2 $\theta$  and  $\phi$  scans. The c-axis of the ZnO film lies in the growth plane; therefore the anisotropic properties parallel to and perpendicular to the c-axis can be utilized. The lattice mismatch along  $[0001]$  ZnO is only 1.53%, whereas the lattice mismatch perpendicular to the c-axis and in the plane of ZnO is 18.3%. Cross-sectional transmission electron imaging shows that the interface between ZnO and R-plane sapphire is atomically sharp and semicoherent. The misfit along the  $[1\bar{1}00]$  direction of ZnO is relieved by a regular array of misfit dislocations with an average spacing of 1.4 nm. The low temperature (11°K) photo-luminescence shows that the FWHM of the excitonic band-edge peak at 3.363 eV is 6 meV, indicating the high quality of the epitaxial ZnO. For surface acoustic wave (SAW) application, the  $(11\bar{2}0)$  ZnO /  $(01\bar{1}2)$   $\text{Al}_2\text{O}_3$  structure offers higher electromechanical coupling coefficient on ZnO surface in comparison to the popular  $(0001)$  ZnO /  $(0001)$   $\text{Al}_2\text{O}_3$  structure. The effective electromechanical coupling coefficient of the Rayleigh type of surface acoustic wave exhibits its maximum in the  $[0001]$  direction. SAW devices were fabricated with wavelengths of 10  $\mu\text{m}$  and 16  $\mu\text{m}$ , and the films' thickness ranged between 0.5  $\mu\text{m}$  to 2  $\mu\text{m}$ . Both Rayleigh mode and Love mode waves were investigated, and higher order wave modes were observed. The acoustic velocities ranged from 4000 m/s to 5600 m/s for the Rayleigh and Love mode waves. Sezawa waves with velocities up to 6500 m/s were obtained. Due to the semicoherent nature of the ZnO/R- $\text{Al}_2\text{O}_3$  interface, a high efficiency transfer of acoustic energy across the interface is achieved, resulting in the high coupling and low loss SAW performance. A strong optical anisotropy exists near the optical bandgap energies due to the different selection rules for light polarized parallel and perpendicular to the in-plane c-axis in  $(11\bar{2}0)$  ZnO /  $(01\bar{1}2)$   $\text{Al}_2\text{O}_3$  structures. For normal incident light linearly polarized 45° with respect to the c-axis, the anisotropic absorption leads to a polarization rotation. The maximum rotation of 10° was achieved at 3.335 eV. This polarization was used to demonstrate the prototype of optically addressed UV light modulator with a high contrast ratio of 70:1.

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# Rotating Disk Reactor-Low Pressure Metal Organic Chemical Vapor Deposition (MOCVD) Production of ZnO and Related Films

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and N. Glumac<sup>2</sup>

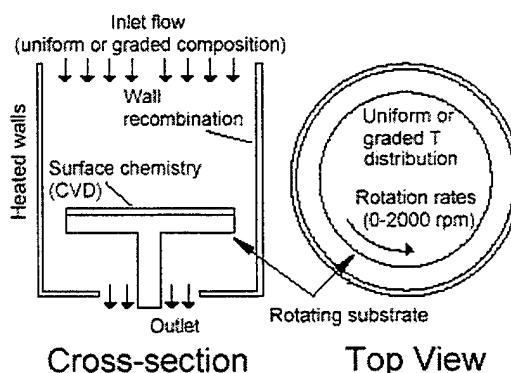
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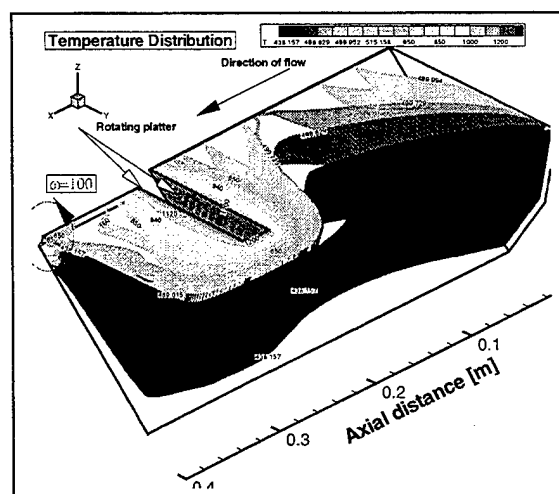
ZnO has several potential and ongoing areas of application; including solar cells, displays, phosphors, lasers, LEDs, opto-electronic devices, and sensors, among others. Application films require uniform working layers, high quality materials, pinhole-free, radiation and other defect free conformal coatings. These desired attributes are generally best achievable by MOCVD. We have mounted a significant effort to develop automated MOCVD systems and process technologies for single and multicomponent oxides.

Our approach is to provide a complete solution by modeling the process and performing the detailed integration of all system components required to insure reproducible high quality film deposition. To efficiently meet materials deposition needs, we have selected to focus on the Rotating Disk Reactor design, operated at low pressure with high speed rotation of the wafer carrier. The modeling provides starting parameters for process optimization. The high rate of rotation of the susceptor results in several beneficial process features. The rotation itself creates a viscous drag that counters the thermal buoyancy effect to produce a non-recirculating laminar driven flow of gases through the system, thus allowing us to functionally separate vapors from their point of injection (oxidizers, precursors and so on) until they mix at the deposition plane in the reactor. This and the lack of recirculation greatly reduce pre-reactions. Further, since the substrate is hotter than the surrounding reactor, thermophoresis drives particles and any potential mist droplets away from the wafer and into the exhausting gas stream. The use of radially symmetric reactant distributing injectors improves thickness and composition uniformity. The geometry is also compatible with an upstream plasma source or may operate in a parallel plate plasma mode. A liquid delivery flash evaporation system, directly integrated with our rotating disk reactor, operating at low pressures, has been developed for use with difficult to evaporate precursors. We also use conventional gas or bubbler

sources as appropriate. Transport line, reactor and exhaust sections are temperature controlled as necessary to prevent condensation or deposition.

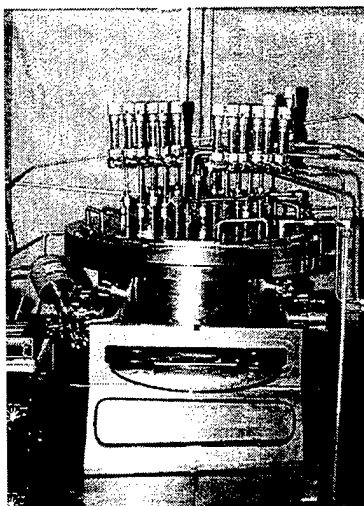


Schematic of rotating disk MOCVD reactor.



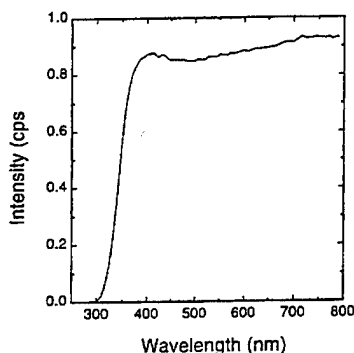
Example of modeling results.

We have applied Metal Organic Chemical Vapor Deposition (MOCVD) to produce an array of ZnO and related films. We have used O<sub>2</sub>, N<sub>2</sub>O and H<sub>2</sub>O vapors as oxidizers and Ar as a carrier gas. We have used N<sub>2</sub>O, NH<sub>3</sub> and N<sub>2</sub> (with and without plasma activation) for N doping, with and without H passivation. We have focused on DEZn, TEGa, TMIn, TMAI, TEOS, TEOG, Mn(cpd), and other metalorganic precursors. Films are typically grown at low pressure, from a few Torr to a few tens of Torr; total flows of a few to several slm, temperatures ranged from ~ 350°C to ~ 650°C, and rotation is typically a few hundred rpm.



Photograph of MOCVD reactor.

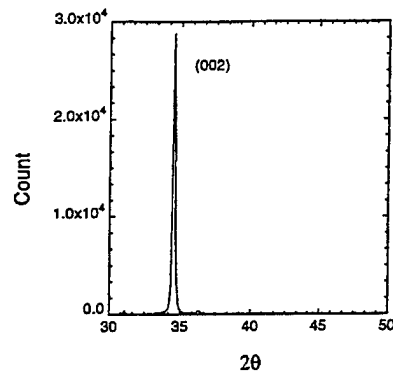
We have produced high purity ZnO films and we have doped them with Ga, In and Al for n-type conductivity, and explored N doping for p-type conductivity. We have also formed zinc germanates and zinc silicates with Mn, Er and other dopants, producing some of the highest brightness low energy electron activated phosphor films reported. We have also grown epitaxial films as buffer layers and ZnO, Al<sub>2</sub>O<sub>3</sub> multilayers. We will present an overview of processes developed and results obtained, including electrical, optical and other physical properties.



Transmission of ZnO.



A digitized video image of a 4" wafer with an electrically stimulated emitting SMI ZnO based EL device.



XRD of ZnO.

<u>SMI Materials Demonstrated</u>	<u>Device Application</u>
ZnO:Ga/Al/In/Ge/Si	TCO, heater (displays)
ZnO:Zn	CL film (displays), diffusion doping
Zn <sub>2</sub> SiO <sub>4</sub> :Mn, Zn <sub>2</sub> GeO <sub>4</sub> :Mn	Green PL, EL, CL film
ZnGa <sub>2</sub> O <sub>4</sub> :Mn/Ga	(displays)
Al <sub>2</sub> O <sub>3</sub>	Insulator
SiO <sub>2</sub> , SiGeO <sub>2</sub>	Dielectric/Insulator
	Green/Blue PL, EL, CL film
CuAgO/CuAlO/CuGaO	p-type TCOs (R&D)
	Alternative TCOs
Cu	Metalization
BST, PZT (in process)	Dielectric

#### Acknowledgments

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## Grain structure and optical properties of ZnO thin films grown by MOCVD

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Recently zinc oxide (ZnO) has been intensively studied as a II-VI semiconductor with a wide band gap of 3.3eV. Potential applications of ZnO include transparent conducting layer, blue light emitting diode (LED), short-wavelength lasers and so on. Optically pumped lasing has been realized in ZnO polycrystalline thin films [1] as well as in powder [2]. The most interesting fact is the feedback mechanism for lasing in ZnO seems totally different from the conventional lasers. According to the experimental results, single-crystal is no longer necessary for laser gain material, which is contrary to usual solid-state semiconductor laser. A "scattering-induced random laser" theory has been proposed by H. Cao et al. to explain the phenomenon. [2]

In order to understand the lasing mechanism of ZnO polycrystalline thin films, systematic studies of the relation between microstructure and optical properties, especially the lasing properties, of ZnO films will be crucial. In this work, ZnO thin films were grown by MOCVD on different substrates, including c-plane sapphire and ITO glass. Diethylzinc was the zinc precursor, and the depositions were carried out in O<sub>2</sub> plasma.

By controlling the growth temperature and film growth rate, ZnO thin films with different grain sizes and crystallinity can be obtained. The grain sizes of polycrystalline ZnO thin films ranged from ~30nm to ~300nm, measured by SEM and AFM. To get the lowest optical pumped lasing threshold, the optimal grain sizes were found to be 50~100nm, outside this optimal range, the pumping threshold increases rapidly.

According to the x-ray diffraction (XRD) results, ZnO thin films grown on c-plane sapphire had c-axis preferred orientation. In theta-2theta scan, only (0002) and (0004) film peaks were present, which indicated a high degree of texture. The crystallinity of the thin films were characterized by the full width at half max (FWHM) of the (0002) peak rocking curve. It has been observed that the lasing threshold is also related to film crystallinity. When the FWHM of (0002) is wider than 1degree, no lasing was observed up to very high pump energy which would damage the film. On the other hand, since narrower rocking curves generally associated with rather large grain sizes, so very narrow FWHM, e.g. 0.1 degree, didn't necessarily lead to very low lasing threshold.

Resistivity was also related to the lasing properties. Conductivity in ZnO thin films is commonly considered to be generated from Zn interstitials and O vacancies. The role of defects in lasing mechanism is still unclear and needs to be further studied.

Based on previous TEM study of ZnO thin films grown by pulsed laser deposition (PLD) and the experimental results mentioned above, a "2-D scattering" model might be possible to explain the lasing mechanism in ZnO polycrystalline thin films, which assume that photons are scattered by grain boundaries between column-shaped grains, and can form a closed path to realize coherent feedback for lasing. More TEM work will be necessary to learn the microstructure of grains, the relation between the grains orientations and lasing threshold, and the distribution of defects, in order to prove the validity of the model.

Refference:

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## ZnO/Mg<sub>x</sub>Zn<sub>1-x</sub>O Quantum Structures

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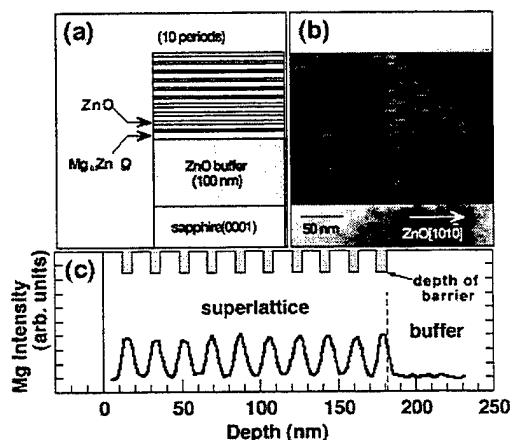
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The observation of room temperature excitonic lasing<sup>1</sup> from ZnO nanocrystalline thin films above very low threshold (24 kW/cm<sup>2</sup>) of optical pumping triggered us to start systematic study of ZnO semiconductor technology including quantum size effect in ZnO based superlattices. Superlattices to be used as an active region in semiconductor light emitting devices enable us to tune luminescence energy and to enhance emission efficiency. Recently, we have reported that wurtzite Mg<sub>x</sub>Zn<sub>1-x</sub>O<sup>2</sup> and Zn<sub>1-y</sub>Cd<sub>y</sub>O<sup>3</sup> alloy films could be prepared by pulsed laser deposition (PLD) to cover the bandgap range from 3.0 eV at y=0.09 to 4.0 eV at x=0.33. Here, we report growth, structural and optical properties of ZnO/Mg<sub>x</sub>Zn<sub>1-x</sub>O quantum wells. Optimization of growth conditions<sup>4</sup>, thermal stability of heterointerfaces<sup>5</sup>, and quantum size effect in photoluminescence (PL) and photoluminescence excitation (PLE) spectra<sup>6</sup> are discussed.

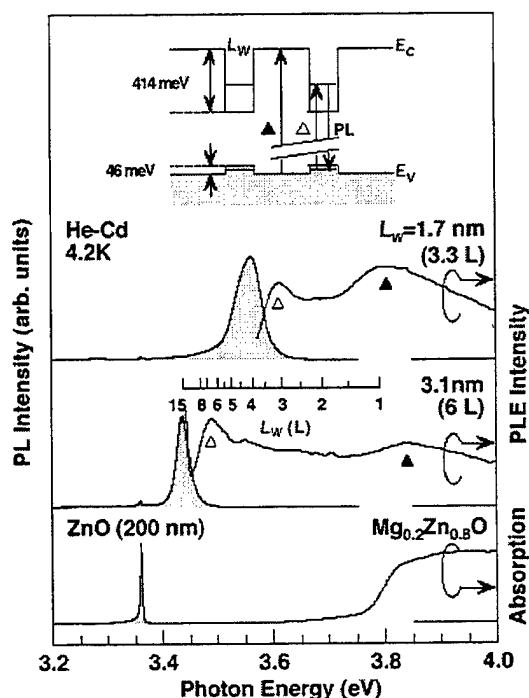
Multi quantum wells (MQWs) (10 periods) were fabricated at 650 °C on 100 nm-thick ZnO buffer layer grown on sapphire(0001) substrates by laser molecular beam epitaxy using pure ZnO and ZnO-MgO mixed ceramic targets. The use of ZnO buffer layers is very useful to reduce surface roughness of Mg<sub>x</sub>Zn<sub>1-x</sub>O alloy films, resulting in the observation of clear X-ray diffraction satellite peaks for MQW samples. Abrupt interface was verified by Auger electron spectroscopy (AES) and transmission electron microscope (TEM) as shown in Fig. 1.

Fig. 2 shows PL and PLE spectra measured at 4.2 K for two of ZnO/ Mg<sub>0.2</sub>Zn<sub>0.8</sub>O MQWs. The PL peak shifts towards higher energy side as well layer thickness ( $L_w$ ) decreases. The two peaks in the PLE spectra are assigned to n=1 quantum sub-band level (open triangles) and barrier layer absorption level (closed triangles), respectively. The positions of the latter peaks agree with the absorption edge for a 200 nm-thick Mg<sub>0.2</sub>Zn<sub>0.8</sub>O film, indicating that the carrier excited at the barrier layers are relaxed into well layers to emit light upon recombination. The observed PLE peak positions for n=1 sub-band level show good agreement with energy position calculated with considering finite potential barrier and assuming the ratio of band discontinuity at conduction band to that at valence band ( $\Delta E_c/\Delta E_v$ ) to be 9. Interface stability against high temperature aging is also reported.

Very recently, we start to grow extremely high quality c-axis oriented ZnO films on lattice-matched oxide substrates.<sup>7</sup> The films showed atomically flat surface, very high crystallinity, excellent electronic properties such as low residual carrier concentration ( $\sim 10^{15}$  cm<sup>-3</sup>) and high electron mobility ( $\sim 100$  cm<sup>2</sup>/Vs), excellent optical properties including low damping rate and efficient stimulated emission. We have also fabricated MQWs on the lattice matched oxide substrates to exhibit much clear quantum size effect. We show the status of ZnO semiconductor technology which is comparable to that for *compound semiconductors*.



**FIG. 1** Cross-sectional schematic (a) and TEM image (b) of a ZnO/Mg<sub>0.2</sub>Zn<sub>0.8</sub>O MQW with  $L_W=5.7$  nm and  $L_B=6.2$  nm. The depth profile of Mg signal intensity in AES was measured for a superlattice with  $L_W=12$  nm and  $L_B=6.2$  nm (c).



**FIG. 2** PL and PLE spectra measured at 4.2 K for two of the MQWs ( $L_W=1.7$  and 3.2 nm). For comparison, PL and absorption spectra of a 50 nm-thick ZnO film and absorption spectrum of a 200 nm-thick Mg<sub>0.2</sub>Zn<sub>0.8</sub>O film are also shown. The ruler in the figure shows calculated quantum sub-band energy as a function of well layer thickness.

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## Optical Spectra of ZnO Films on Lattice-Matched Substrates Grown with Laser-MBE

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Recently, much efforts are devoted on the study of ZnO film. The wide gap semiconductor ZnO whose band-gap energy is approximately 3.4 eV has been recognized as an important candidate for novel semiconductor lasers. When ZnO thin-films are grown on sapphire substrates which are largely lattice-mismatched (18 %), formation of hexagonal nanocrystals make low-threshold lasing possible even at room temperature. For achieving the laser-diode, however, fabrication of defect-free crystalline films is the critical task to be solved. We have tried to grow it on  $\text{ScAlMgO}_4(0001)$  (SCAM) substrates whose lattice-constant matches that of ZnO with 0.12 % using laser-MBE method. Crystallographic quality became better than sapphire substrates. Spectra such as transmission or reflection have been measured for elucidating the basic optical-properties of not only undoped-ZnO films on SCAM substrates but also quantum wells based on  $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ .

The films are grown with thickness ranging 28 nm through 55 nm, a deposition temperature of about 550 degree C, and an oxygen pressure of  $10^{-6}$  Torr. They have c-axis orientation. The transmission spectrum on SCAM at 6 K has two well-resolved peaks both of which are attributed to resonances of A-(367.0 nm) and B-excitons (366.3 nm), respectively. This splitting can be observed at the temperature up to 150 K. On the contrary, it is difficult for ZnO on sapphire to distinguish these peaks even at 2 K because they are close in energy and because of large non-radiative damping-constant of excitons. It can be estimated that oscillator strength of B-exciton is five times larger than that of A-exciton. This is, to our best knowledge, the first observation of exciton absorption and direct estimation of parameters related to A- and B-excitons. These parameters have been so far deduced only indirectly by analyzing excitonic reflection spectra because bulk crystals were excessively thick. Reflection spectra of this film exhibit the two oscillator-structures arisen from the exciton resonances.

The sharp-peak structure reflects small damping-constant, which supports the high crystallinity of the film improved by lattice-matched SCAM substrates. We also on the optical properties of quantum well structure as well.

## Plasma assisted MBE growth and their characteristics of ZnO layers and related heterostructures

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In 1996, we decided to start a ZnO project, since ZnO has so many attractive properties including large exciton binding energy, large LO phonon energy, large bond length. The listed below is our recent publications on ZnO, where refs 1 -3 deal mainly with plasma-assisted MBE growth of ZnO on sapphire substrates and characterization of their structural, optical properties. In particular, ref 3 shows the self-organized formation of ZnO quantum pyramids. One of the remarkable features of ZnO films was the excellent photoluminescence properties, which was more than expected. Strong and sharp bound excitonic emission at 3.36 eV dominated low temperature PL with negligible small deep level emission. Using such high quality ZnO layers, refs 4 - 7 present the first demonstration of optically pumped excitonic lasing at room temperature (refs 4, 6), high temperature stimulated emission up to excitonic mechanism up to 550K, and high temperature stability of the threshold intensity for stimulated emission (ref 7). Those high excitation optical experiments have been performed on ZnO films grown on sapphire substrates. Very recently, we have studied in more detail on the stimulated emission mechanisms based on pump-probe experiments (A. Yamamoto et al, submitted to APL).

Since the large lattice misfit between ZnO and sapphire substrate imposes a limit in crystal quality, we have extensively examined various substrates including CaF<sub>2</sub>, spinel, GaN epitaxial layer, and ZnO substrates for ZnO epitaxy. Through extensive work on growth and characterization of ZnO layers, we have achieved ZnO growth in layer-by-layer mode which was verified by RHEED intensity oscillations. It is found that the crucial point to obtain high quality layers is the control of the interface as indicated by TEM study. We have correlated the interface chemistry and structure as characterized by TEM and local chemical analysis and the structural and optical properties. Some of our ZnO layers show well resolved free excitonic emission at low temperature in addition to

the very sharp bound excitonic emission (1.5 meV) at 3.36 eV. Extensive XRD shows that the film quality is basically determined by the quality of the substrate. We are studying highly excited optical properties of such high-quality ZnO layers for a wide temperature range.

In the mean time, we have tried to grow heterostructures of ZnMgO/ZnO/ZnMgO and ZnO/ZnCdO/ZnO heterostructures. Since MgO and CdO are of rock salt structure, the growth of ZnMgO and ZnCdO were found to be problematic. Nevertheless we have grown those heterostructures by plasma-assisted MBE and have characterized the heterostructures by PL, cathodoluminescence, TEM, XRD, and AFM.

In conclusion, we have demonstrated the growth of high-quality ZnO layers by controlling the interfaces between the substrates and the ZnO epilayers. Heterostructures of ZnMgO/ZnO/ZnMgO and ZnO/ZnCdO/ZnO have been grown and their optical and structural properties have been assessed.

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## Plasma assisted molecular beam epitaxy for ZnO based II-VI semiconductor oxides and their hetero-structures

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The desire to produce short wavelength lasers diode (LD) has motivated research into wide bandgap semiconductors such as ZnSe and GaN. The excitonic nature of these materials has proved to be of particular interest because of its potential application to low threshold LDs. However, for these effects to be of practical value excitons must survive at room temperatures (RT). Unfortunately, without significantly enhancement of binding energies the excitons of ZnSe and GaN can not be efficiently utilized at RT. One of the most promising alternatives to ZnSe and GaN based material systems in this regard is ZnO based II-VI semiconductor oxides. ZnO has a bandgap of 3.37 eV at RT and the exciton binding energy of 60 meV ensures excitonic survival well above RT. Furthermore, by using quantum structures, the binding energy of the excitons and the oscillator strength can be greatly enhanced, even excitonic processes such as a radiative recombination of biexcitons could be expected to play a role in the laser gain at RT.

However, reliable epitaxial growth techniques for high quality ZnO films and ZnO based hetero-structures are still in developing. Here, we report our recent advances in plasma assisted MBE of ZnO films on Al<sub>2</sub>O<sub>3</sub> (0001) substrates and GaN/Al<sub>2</sub>O<sub>3</sub> epilayer substrates.

In the case of Al<sub>2</sub>O<sub>3</sub> (0001) substrate, due to the very large lattice mismatch (18%) and crystallographic mismatch, columnar growth usually occurs instead of two-dimensional epitaxial growth. In order to surmount this obstacle, a novel buffer structure is introduced. By using the buffer, atomically flat surface is obtained, which results in the observation of RHEED oscillation. RHEED oscillation lasts more than 30 periods. The surface kinetics was studied and optimized growth conditions were determined. ZnO films grown by plasma assisted MBE indicate satisfactory quality. XRD rocking curve of the (0002) diffraction peak has a typical FWHM less than 50 arcsecond. Low temperature photoluminescence shows that bound exciton at 3.365 eV with a FWHM about 3 meV dominates the spectra, while free exciton E<sub>A</sub> and E<sub>B</sub> can be observed at 3.377 eV and 3.383 eV respectively. Deep level emissions are two orders less intense than the excitonic ones. Room temperature Hall measurement indicates a carrier concentration around  $2 \times 10^{16} \text{ cm}^{-3}$  and electron mobility around  $100 \text{ cm}^2/\text{Vs}$ .

In the case of GaN/Al<sub>2</sub>O<sub>3</sub> epilayer substrates, a pre-treatment is used to prevent the Ga terminated surface of MOCVD grown GaN epilayer from oxidation. The initial growth status was studied by AFM and TEM. It was found that the stepped terrace structure and dislocation related pits on the surface of GaN epilayer influence the ZnO growth from the initial stage. The TEM and HR-XRD measurements show that dislocations in ZnO epilayer are dependent on that within the underneath GaN film. Because of the small lattice mismatch (1.8%), which reduces the strain effects, fine excitonic emission peaks, including free excitons and several bound excitons can be well resolved in low temperature photoluminescence.

MgZnO/ZnO and CdZnO/ZnO hetero-structures were also grown by plasma assisted MBE. RHEED oscillation was used to real time control the composition and thickness of the multi-layers. Structural and optical properties of these hetero-structures will also be reported.

## DIFFUSION OF OXIDE IONS IN ZINC OXIDE CERAMICS AND THIN FILMS

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Metal-oxide varistors used in surge arresters or varistors are ZnO-based ceramic semiconductor devices with highly nonlinear current-voltage characteristics similar to back-to-back Zener diodes, but with much greater current-, voltage-, and energy-handling capabilities[1,2]. Such materials are characterized by their non-uniform grain size, porosity, secondary phase distribution, impurity segregation and grain-grain disorientation. The electric properties of ZnO varistors are, furthermore, known to be greatly influenced by the grain-boundary diffusion of oxide ions and the defect of ceramics.

Non-doped single crystals were grown by evaporation. Single crystals doped with Mn, Co, and Al ions were grown by a flux method. ZnO based ceramics prepared by a hot-isostatic-pressing were used for oxygen diffusion experiment[3]. The diffusion coefficient was determined by solid-gas exchange, using  $^{18}\text{O}$  as tracers[4].  $^{18}\text{O}$  diffusion profiles were measured with a SIMS (CAMECA, IMS4f), using  $\text{Cs}^+$  as primary ions. The 3D-analysis of isotope were carried out by means of a planar detector(C.Evans: RAE).

The results are interpreted as indicating extrinsic behavior. The values of the lattice diffusion coefficients with higher valence dopants compared with zinc ions are greater than lower valence dopant such as lithium ions. This fact suggests that the diffusion mechanism of lattice oxygen diffusion is one kind of the interstitialcy, while the oxygen diffusion was controlled by the vacancy mechanism in some case of a thin film. We believe that two kinds of mechanisms coexist in the zinc oxide.

Furthermore, using the data at deeper depth, the grain boundary diffusivities of oxide ions were also evaluated. Although the lattice diffusion coefficients varied by two orders of magnitude, the products of grain boundary width and grain boundary diffusion coefficient were less sensitive to the type of dopants.

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## Susceptibility of the *C*-axis Orientation of Polycrystalline ZnO Thin Film on the External Electric Field

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Zinc oxide has a wurtzite-type structure with a 6-mm symmetry. Because of its crystal symmetry, if the *c*-axis of each polycrystallite and its crystallographic polarity are in the same direction, then the polycrystalline film has the same piezoelectric and other crystallographic properties as the single crystal of ZnO. Polycrystalline ZnO films have been used extensively as piezoelectric transducers for generation and detection of surface and bulk acoustic waves at microwave frequencies. In order for polycrystalline film to emulate the electromechanical coupling behavior of a single crystal, along with high resistivity and proper stoichiometry, the normals to the basal planes of the crystallites within the ZnO film must be predominantly oriented perpendicular to the plane of the substrate (*c*-axis normal orientation). In this regard, the crucial factor for ZnO piezoelectric device performance is the degree of preferred orientation.

Two methods, direct and indirect, were utilized to produce zinc oxide thin films. In the direct method, reactive evaporation, oxygen was introduced into the zinc vapor stream and ZnO films were deposited on cold substrates in a vacuum system. Parallel electric fields, detached electrodes, were applied during the reaction process. It was observed that the electric field had no effect on the preferred *c*-axis orientation of the ZnO crystals. There was no significant difference in the crystal size or surface texture of ZnO samples subjected to electric fields with respect to the sample that experienced no electric field.

In the indirect method, oxidation, first a thin layer of zinc was deposited on the surface of the substrate in a vacuum chamber and then the sample was oxidized in air under the influence of an applied electric field. Perpendicular and parallel electric fields, detached electrodes, were applied at different oxidation temperatures.

Perpendicular, normal, electric fields were applied in two opposite directions, namely positive and negative. The positive field was defined when the sample was positive (anode) and negative field was defined conversely. The application of positive fields at 550°C improved the *c*-axis orientations up to 1000 Vcm<sup>-1</sup>. Further increase in field strength caused the *c*-axis orientation to decline to its original value (no applied field). The application of negative normal fields at 550°C deteriorated the *c*-axis orientations up to 800 Vcm<sup>-1</sup>. The *c*-axis orientations improved to its original value by increasing the field strength greater than 800 Vcm<sup>-1</sup>. The crystal size remained unchanged, but the surface morphology was affected by the application of the electric fields at temperatures above the melting point of zinc. No significant change in optical properties was detected for samples that were subjected to electric fields. Whenever the *c*-axis orientation improved, crystals on the film surface became rounded and a more ordered microstructure was observed. On the other hand, the deterioration of *c*-axis orientation was manifested by the increase in the number of whisker-shaped crystal needles on the surface of the ZnO thin films.

Parallel electric fields were also applied during the oxidation of zinc thin film. We observed that the oxidation temperature should be higher than the melting point of zinc (420 °C) to see any change in the film orientation due to the application of an electric



field. The *c*-axis orientation improved by increasing the strength of the field. It was observed that the number of needle-dendrite-shaped crystals on the surface of the film under the applied field of  $1000 \text{ Vcm}^{-1}$  was reduced. Furthermore, the *c*-axis orientation of this film was improved compared to the *c*-axis orientation of the reference sample oxidized without any applied field. We estimated the crystallite size by measuring the peak width at half maximum of the 002 reflection peaks. The crystallite size was not influenced by the application of the field and remained around 17.1 nm for the samples oxidized at 600 °C, and 17.5 nm for the samples oxidized at 650 °C. The films' resistivities improved slightly with the application of electric fields. No change in optical transmittance was observed for the samples oxidized at a certain temperature under the influence of the electric field. ZnO films were translucent with the average transparencies of 62% at 700 nm wavelength. The optical band gap was estimated to be 3.28 eV for the samples oxidized at 650 °C. The photoluminescence characteristics of the films were not influenced by the external field for either oxidation temperature.

## **Valence Band Ordering in ZnO**

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There has been a long standing controversy over the symmetry ordering of the valence bands in ZnO. ZnO crystallizes stably in the wurtzitic modification and the wurtzitic band structure was first derived by Birman (1). The zone-center conduction band is s-like having  $\Gamma_7$  symmetry. The valence band is p-like, splitting into three doubly degenerate bands due to spin-orbit and crystal-field interactions. The top valence band, A, has  $\Gamma_9$  symmetry while the two lower valence bands, B and C, have  $\Gamma_7$  symmetry. The fundamental exciton spectra of ZnO crystals were first investigated by Thomas (2). From reflection spectra, he identified three exciton series, one associated with each of the three valence bands. From polarization studies of both reflection and absorption spectra, Thomas concluded that states from the first and third valence bands were mixed and that the symmetries of the two top valence bands were reversed with respect to the usual ordering of the wurtzitic band structure.

A later study of the exciton structure in ZnO was conducted by Park, et al.(3). The essential difference between the work reported by Park, et al. (3) and that of Thomas (2) was spectral peak assignments. The line interpreted by Thomas as the intrinsic ground state A – exciton transition was interpreted by Park, et al. as an extrinsic, ionized donor bound exciton complex transition. Thus, from their studies, Park, et al. concluded that the valence band symmetry ordering in ZnO was not reversed, as was claimed by Thomas.

High quality ZnO crystals have been grown by vapor phase and hydrothermal methods. Some hydrothermally grown crystals contain in-grown strains. These strains result in energy shifts of the free excitons as well as relaxation of the selection rules. In the standard wurtzite structure the conduction band has  $\Gamma_7$  symmetry while the top

valence band has  $\Gamma_9$  symmetry, and the next two lower valence bands have  $\Gamma_7$  symmetry.

Exciton symmetries associated with optical transitions between these bands are as follows:

$$\Gamma_7 \times \Gamma_9 \rightarrow \Gamma_5 + \Gamma_6$$

$$\Gamma_7 \times \Gamma_7 \rightarrow \Gamma_5 + \Gamma_1 + \Gamma_2$$

The  $\Gamma_5$  and  $\Gamma_1$  excitons are allowed while the  $\Gamma_6$  and  $\Gamma_2$  excitons are forbidden; also the  $\Gamma_5$  and  $\Gamma_6$  excitons are doubly degenerate while the  $\Gamma_1$  and  $\Gamma_2$  excitons are singly degenerate. In strain-free crystals, the selection rules are relaxed in the presence of an applied magnetic field allowing the forbidden excitons to be observed. In hydrothermally grown crystals containing strain a forbidden exciton is observed in appropriate polarizations without an applied magnetic field. Also, in second order (which gives higher resolution) this exciton shows line splitting due to strain. The forbidden exciton also splits in the presence of an applied magnetic field. This allows the identification of the unallowed exciton as a  $\Gamma_6$  exciton rather than a  $\Gamma_2$  exciton since the latter is a singlet and would not split. These data are therefore consistent with the top valence band in ZnO having  $\Gamma_9$  symmetry.

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## ELECTRONIC BAND STRUCTURE OF ZnO AND RELATED $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ALLOYS

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The ordering of the topmost valence band states in ZnO has been controversial for several decades. The ordering found in most wurtzite semiconductors is  $\Gamma_9, \Gamma_7, \Gamma_7$ . However, in ZnO the ordering according to Thomas (1960) appeared to be  $\Gamma_7, \Gamma_9, \Gamma_7$  which indicates a negative spin-orbit coupling parameter. This was later disputed by Park et al. (1966). Recently, Reynolds et al. (1999) revisited the problem and confirmed Park's model. In this paper we present the results of first-principles calculations of the band structure using the linear muffin-tin orbital method including spin-orbit coupling effects. We find that the sign of the spin-orbit coupling depends sensitively on the interaction with the Zn3d states and is in fact negative when the local density approximation is used for exchange and correlation. However, it is well known that this approximation underestimates the binding energy of the Zn3d bands because of the incomplete cancellation of the self-interaction in the LDA. It also affects the crystal field splitting. In order to mimic a more correct treatment of exchange and correlation, we also performed calculations including a semi-empirical shift of the Zn3d bands. It is found that when the Zn3d bands are shifted such as to produce a correct crystal field splitting, the spin-orbit splitting still comes out negative. The position of the Zn3d bands is then still slightly above the experimentally found position but this is expected because in a GW quasiparticle calculation, one expects the self-energy operator to be energy dependent. This implies that one cannot expect a single energy-independent Hamiltonian to provide both the valence band maximum and the Zn3d bands as eigenvalues. To resolve the discrepancy with experiments, we note that the recent experimental evidence for the valence band states is in fact indirect and based on the excitonic exchange splittings and their dependence on magnetic field. However, in view of the close energetic spacing of the valence band levels, it is important to take into account the coupling between the excitons associated with the different band edges. This problem needs further investigation.

The second part of our presentation is concerned with  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  alloys. The latter are of interest from the point of view of using them as barrier material for fabricating ZnO quantum well structures. Recently the growth of wurtzitic  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  alloys was reported by Ohtomo et al. (1998). Pure MgO prefers the rocksalt structure. Therefore one cannot easily estimate band gap bowings in this alloy system

and the question arises whether the  $\text{Mg}_x\text{Zn}_{1-x}\text{O}$  alloys are in fact stable. To this end and to estimate the relative stability of the two crystal structure modifications as a function of concentration, we perform a theoretical study of the band structures and total energies of ZnO, MgO in the wurtzitic and rocksalt based structures using the full-potential linear muffin-tin orbital method and the local density approximation. We find that when the symmetry of MgO is restricted to be wurtzitic, the internal structural parameter relaxes to  $u = 1/2$ , meaning that the basal plane layers become entirely flat. This implies essentially a five-fold rather than 4-fold bonding, because the two neighbors in the c-direction are at equal distance from the Zn atom. This bond is slightly larger than the in-plane one, so one can also view the structure as 3-fold bonded with a second nearest neighbor pair of bonds very close in distance to the nearest neighbors. In fact, the structure is thus formally equivalent to that of h-BN, but with the important difference that the interplanar spacing is very small and strongly bonded instead of weakly bonded, as is the case in h-BN. It is indicative of the tendency for ionic materials to prefer a higher coordination than 4-fold. This structure can now be transformed into the rocksalt structure by a simple compression in the basal plane. We investigated the total energy along this transformation path and found that there is indeed a small barrier between the relaxed wurtzitic phase above described and the rocksalt phase. Thus, the former can be considered to be metastable. The above raises questions about the structure of intermediate compositions.

In order to estimate the band-gap behavior in the alloy system, we have used the cubic zincblende structure as first approximation and used one intermediate composition  $\text{MgZnO}_2$ . In that case, these relaxation effects do not come into play. In nitride alloy systems, it was found that the zincblende and wurtzite band gap bowings are very similar. We include a quasiparticle band gap correction based on the known experimental band gap of MgO in the rocksalt and ZnO in the wurtzite structure, assuming that gap corrections are structure independent. This leads to a band gap bowing coefficient of 0.56 eV and a variation of the band gap from 3.4 eV in ZnO to 6.25 eV in MgO, indicating a gap of 4.2 eV for a 33% MgO composition, the maximum MgO content presently attained in the crystal growth before phase separation of rocksalt MgO occurred. This is in excellent agreement with the data of Ohtomo, but requires further work to investigate the effects of the wurtzitic local relaxations.

## Electrical and Optical Properties of Point Defects in ZnO

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It has long been assumed that the electrical and optical properties of ZnO are controlled by native defects, in particular, the O vacancy  $V_O$  and/or the Zn interstitial  $Zn_i$ . However, very few controlled experiments have tested this important hypothesis. With the recent availability of large, high-quality, single-crystals of ZnO, it is now possible to use high-energy electrons to create relatively small concentrations of isolated point defects and observe their effects on the electrical and optical properties of these crystals. The ZnO crystals used in this study were grown by Eagle-Picher, Inc., and had 300-K and peak Hall mobilities of about 225 and 2000  $\text{cm}^2/\text{V}\cdot\text{s}$ , respectively, and photoluminescence (PL) donor-bound-exciton linewidths of  $< 0.3$  meV. Temperature-dependent Hall-effect (TDH) analysis yielded two donors, with approximate energies 30 and 60 meV, and concentrations  $1 \times 10^{16}$  and  $1 \times 10^{17} \text{ cm}^{-3}$ , respectively, and an acceptor concentration of  $2 \times 10^{15} \text{ cm}^{-3}$ . The conclusions, so far, are the following:

1. For c-axis irradiation, electrons directed at the Zn face of n-type material produce damage at a higher rate than those directed at the O face. Also, it appears that simple, nearest-neighbor Frenkel pairs (such as  $V_{Zn}-Zn_i$ ) are not stable, because the positively-charged  $Zn_i$  will immediately recombine with the negatively-charged  $V_{Zn}$ . In fact, stability is found only in larger, "chain-like" defects, such as  $V_{Zn}-Zn_O-O_{Zn}---Zn_i$ , especially if the  $Zn_i$  has sufficient kinetic energy to drift away from the rest of the complex. The defect-donor energy is about 30 meV, which is the same as that usually observed in the as-grown material; thus, it is probable that the dominant native donor is a  $Zn_i$ -related defect, rather than one involving  $V_O$ . The defects anneal out at about 325 °C, well described by a first-order process with an activation energy of 1.73 eV.
2. The production of the chain defect mentioned above requires a high electron energy, at least 1.6 MeV. Thus, ZnO is more "radiation hard" than some of its counterparts, such as Si, GaAs, and even GaN, and might be useful in high-radiation environments, such as those encountered in space.
3. Electron irradiation also affects the photoluminescence (PL) intensity less in ZnO than in those other semiconductor materials. For example, the overall PL intensity decreases by less than a factor two after a 1.6-MeV,  $4 \times 10^{16} \text{ cm}^{-2}$  irradiation. This fact suggests that non-radiative centers are not easily formed, and thus, that photonic applications will also fare well in high-radiation environments.

## Microstructural evolution of radiation-induced defects in ZnO during isochronal annealing

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In this study we present the microstructural changes in ZnO after electron or proton irradiation and the thermal evolution of the radiation induced defects during isochronal annealing. The nominally undoped samples, grown under different conditions, were irradiated either with 2 MeV electrons at 70 K to a fluence of  $5 \times 10^{17}$  e/cm<sup>2</sup> and  $5 \times 10^{18}$  e/cm<sup>2</sup> or with 3 MeV protons at 223 K to a fluence of  $1 \times 10^{18}$  p/cm<sup>2</sup>, respectively. Positron lifetime and Doppler broadening measurements were performed to investigate the thermal stability of the radiation induced defects as well possible clustering mechanisms during isochronal annealing. After electron irradiation at higher doses a significant defect component was observed which can be attributed to annihilations in monovacancy-type defects. Proton irradiation reveals a significantly different defect picture. Isochronal annealing causes agglomeration to larger defect complexes. The observed annealing stages are related to the annealing of variously sized vacancy complexes.



## Sources of $n$ -type conductivity in ZnO

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Zinc oxide almost always exhibits strong  $n$ -type conductivity. Despite years of investigations, the source of this conductivity is still controversial. Because of its prevalence, the  $n$ -type conductivity has traditionally been attributed to native defects. A recent first-principles investigation [1], however, revealed that none of the native defects has characteristics consistent with a high-concentration shallow donor. The dominant native defects are vacancies: Zn vacancies are favored in oxygen-rich material, and act as deep acceptors; oxygen vacancies occur in zinc-rich material, and do act as donors – however, they are far from shallow. The only defect that behaves as a shallow donor is the ZnO antisite; however, its formation energy is quite high, and it is therefore unlikely to form during growth. High-energy defects *can* be formed during irradiation, however, and it is possible that the ZnO antisite is the defect observed in the recent electron-irradiation experiments of Look *et al.* [2].

If the prevailing  $n$ -type conductivity is not due to native defects, it must be attributed to impurities which are unintentionally incorporated. Based on first-principles density-functional-pseudopotential calculations, we find that hydrogen is an excellent candidate for such an impurity. Hydrogen is ubiquitous, and very difficult to remove from the crystal growth environment. It also forms a strong bond with oxygen, providing a powerful driving force for its incorporation in the ZnO crystal. Interstitial hydrogen in ZnO occurs in the positive charge state, and its donor level is a resonance in the conduction band. While hydrogen in other semiconductors is an amphoteric impurity, always assuming a charge state that counteracts the prevailing doping of the material, hydrogen in ZnO behaves exclusively as a donor, and strongly dopes the material.

The interaction between hydrogen and oxygen responsible for the strong donor behavior of interstitial hydrogen can be viewed as follows: hydrogen binds so strongly to the oxygen anion, and with such a short bond length, that the O-H entity can practically be regarded as a single unit. The addition of the hydrogen is then equivalent to adding a proton to the oxygen, causing it to electronically behave like a fluorine atom, which is a donor in ZnO.

The consequences of this proposal for experimental observations of  $n$ -type conductivity in ZnO will be discussed, as well as the relation of these findings to previous experiments on hydrogen in ZnO.

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## ABSTRACT

## Luminescence Properties of ZnO Doped with Rare Earth.

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The photoluminescence, cathodoluminescence, time resolved spectra, and their kinetics of ZnO sintered pellets, bulk crystals, and epilayer (growth on a sapphire) doped with Nd, Sm, Dy, Er, Tm and Yb and co-doped with Li were studied. The ZnO bulk crystals and epilayers were doped with rare earth by implantation. The implanting ion beam was inclined at  $10^\circ$  to the normal of the ZnO epilayers to prevent channeling. Samples were given isochronal thermal annealing treatments at different temperature and duration. The PL was investigated at temperatures ranging from 9-300 K by excitation above and below the bandgap with different excitation intensities using CW and pulse excitation by a He-Cd, Ar<sup>+</sup> ion lasers and Continuum Sunlite tunable laser. The PL spectra of ZnO: RE<sup>+3</sup> excited above and below the bandgap and CL spectra showed the characteristic emissions of the rare earth ions. The PL and CL kinetics (rise and decay) was studied for different emission lines as a function of temperature and excitation intensity. The experimental results are discussed and analyzed using proposed theoretical models for rare earth ion excitation and luminescence kinetics. Finally, because ZnO is a suitable substrate for GaN growth (close lattice match), we also discussed the possible applications of ZnO doped with rare earth as a promising material for a ZnO(n)-GaN(p) heterostructure for light emitting devices.

## Nonlinear Optical Properties of ZnO

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### Abstract

We report third-order nonlinear optical properties of undoped single crystals of the wide bandgap semiconductor ZnO. The ZnO crystals were grown at the Sensors Directorate of the Air Force Research Laboratory using the hydrothermal method. The crystals are of high optical quality and are transparent in the visible part of the spectrum. The contributions of the real and imaginary parts of the third-order nonlinear optical susceptibility were studied using the Z-scan technique. The Z-scan experiments were carried out using 30 picosecond pulses at 532 nm wavelength obtained from a frequency doubled Nd:YAG laser. The measurements were obtained with the electric field polarization of the laser light oriented orthogonal to the crystal c-axis. The nonlinear refractive index of the crystals is found to be negative. The ZnO samples exhibit two photon absorption and high damage thresholds. Our results indicate that the ZnO crystals may be good candidates for applications in optical power limiting of high peak power pulses due to the combination of self-defocusing and two photon absorption. We observe a high degree of pulse stabilization when the crystals are placed at the output of a highly fluctuating high power laser. Time resolved degenerate four-wave mixing (DFWM) experiments were carried out using 30 picosecond pulses at 532 nm wavelength. The DFWM experiments were carried out using a backward wave geometry. The DFWM measurements indicate an ultrafast response followed by a slower mechanism. We observe a third-order dependence of the phase conjugate signal intensity with the variation of the total input intensity for zero delay between the interacting beams in the DFWM experiments and a higher order dependence when the backward pump beam is delayed 200 picoseconds with respect to the forward pump and probe beams. The higher order effect is attributed to a change in index due to carriers generated via a multiphoton excitation.

# Electron Pumped Ultraviolet Super-radiation Luminescence from Sputtering ZnO Film

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**Abstract** We report the observation of the cathode-ray (CR) pumped ultraviolet (UV) super-radiation luminescence in ZnO thin film at room temperature (RT) for the first time. The dependence of UV (peak at about 390nm) and green (peak at about 520nm) luminescent peaks of ZnO thin film under CR excitation on excitation electron beam current has been investigated. With the increase of the intensity of excitation electron beam current, green peak relatively decreases and UV peak relatively increases, so that the luminescent color of ZnO changes from green to blue-purple. The green peak intensity increases sublinearly with the increase of the intensity of electron beam current and saturates by a relatively low intensity of electron beam current. But the intensity of 390nm ultraviolet peak increases superlinearly with the increase of the electron beam current intensity. This is an ultraviolet super-radiation luminescence of exciton in ZnO under high density electron pump. In this work, three dimension atomic force microscope images of the surface of unannealing and annealing ZnO film are given.

For some time there has been great interest in wide band-gap semiconductors, in particular, there is strong commercial desire to produce efficient and lasing blue light emitting diodes and short-wavelength laser diodes. Over the last few years, research efforts were focused on the blue light emitting diode GaN and the blue light emitting laser diode ZnSe, and have made substantial progress in recent years.

In 1997 a new type of chip-based laser on zinc oxide that generates the shortest wavelength light — ultraviolet (UV) was announced <sup>[1-2]</sup>. The new laser, based on the semiconductor zinc oxide (ZnO), promises even greater gains for packing far more information into compact (CD), and CD-ROM (read only memory). A similar results of optically pumped lasing of ZnO by Nd:YAG laser excitation was also reported <sup>[3]</sup>.

ZnO, a direct band material having hexagonal structure, has band gap of 3.24 eV (at RT) or 3.37 eV (low temperature at liquid nitrogen). One particularly interesting feature is the high exciton binding energy which, at 59 meV, should ensure that the excitons in ZnO are not ionized and excitonic emission mechanisms are significant at temperature well above RT. Under the high intensity optical pumping (higher than 240 kW/cm<sup>2</sup>) by the frequency-triplet output (355nm) of a Nd:YAG laser or by the 325nm line of a cw He-Cd laser (325nm) the ultraviolet lasing emission of ZnO thin film is observed at RT by the following evidences: By increasing of the excitation intensity above a threshold the rapid growth of the emission peak intensity occurs, the spectral width of the emission peak is narrowed and the wavelength of the peak is shifted to red direction, and the emission peak is polarized <sup>[1,3]</sup>. The authors of the Ref.1 found that the surface of ZnO thin film is consists of honeycombl like pattern with width about 50 nm. They believe that the reflective cavities for producing the laser light of ZnO thin film are the boundaries of that honeycombl like structure. But the statement of the boundaries becoming the laser resonant cavity is only an estimation.

We notice that in recent announcement of having detected laser light emission from ZnO thin film the photon pump method was used for excitation. In this work, we would like to use electron beam to pump the ZnO thin film. The cathodoluminescent (CL) spectra of ZnO thin film have been studied. Under CR excitation at RT, with the increase of excitation density of electron beam current the UV emission increases and the green emission decreases relatively. So that the color of emission light of ZnO thin film changed. And a super-radiation luminescence phenomenon of UV light from ZnO thin film has been observed at RT for the first time.

ZnO thin films were prepared by reactive dc sputtering on the surface of Si (100) substrate. After sputtering, samples were annealed in air at 800 or 1000°C for 1h (the detail refers to Ref.4). The samples of ZnO thin film are highly orientation hexagonal crystal film having the thickness about 200nm. A set of three-dimension Atomic Force Microscope (AFM) images of the surface of ZnO thin film on Si (100) substrate before and after annealing were detected by Dimension 3000 Scanning Probe AFM (Digital Instruments Company, USA). We can see the surface of ZnO

thin film before annealing is smoothly and the fluctuation is about 10 nm, and the width of the surface islands is about 100 – 300 nm. But the surface of ZnO thin film after annealing has a lot of parallel whisker crystals of ZnO which having width about 0.1 – 2  $\mu\text{m}$  and the height about 10 – 200 nm are grown up from the surface. It shows that the ZnO film has obviously growth along c-axis perpendicular to the surface. This result is agree with the x-ray diffraction analysis: the full width at half maximum (FWHM)  $0.65^\circ$  (before annealing) of diffraction peak (002) at  $2\theta$   $34.21^\circ$  in ZnO on Si (100) substrate is reduced obviously to  $0.2^\circ$  (after annealing at  $800^\circ\text{C}$  for 1h) (see our previous paper Ref.4). The FWHM reduction means that the grains in the surface grew up.

The luminescence of ZnO thin film was measured by YFC-1 type Phosphor CL Measurement Instrument which has excitation conditions as follows: anode acceleration voltage 2-50kV, electron beam current 0.002-10 $\mu\text{A}$ , and bombardment electron spot area  $1\text{mm}^2 - 1\text{cm}^2$ . The samples of ZnO film after annealing at 800 -  $1000^\circ\text{C}$  for 1h in air emit bright wide band green light (peak at about 520nm) and UV light (peak at about 390nm) under the CR excitation. With the increase in the electron beam current density the UV emission increases and the green one decreases relatively, so that it results the emission light color of ZnO from green to blue and even purple. A set of spectra of ZnO film under high density CR excitation at 2, 5 and 10kV,  $\phi 2\text{mm}$  and the electron currents from 0.06 to 3.0  $\mu\text{A}$  have been measured. A superlinear dependence of 390nm UV emission intensity of ZnO on electron beam current density was determined, which shows that the higher density electron excitation used, the more efficiency 390nm UV light emit. This is that a phenomenon of superlinear luminescence of ZnO thin film occurs at RT under CR excitation. But under same excitation conditions the 520nm green band does not obey this law. Opposite to this, the intensity of 520nm green band obeys the sublinear increase law and saturates at not very high excitation current density. We can suggest that the luminescent centers of UV and green light of ZnO come from different origins.

In order to discuss the luminescent mechanism of ZnO thin film under CR excitation, we notice that the ZnO thin film samples sputtered on Si substrate will not give light emission before annealing process and only the sample after annealing above  $800^\circ\text{C}$  in air for 1h having good hexagonal structure grown along c-axis can emit green and UV light. Higher temperature annealing is helpful to crystallization of ZnO film. Better crystallized ZnO film will emit with higher brightness and its UV light is stronger than that of the green one. Then we can suggest that the luminescent mechanism of ZnO film as follows: the green emission comes from the vacancy of the oxygen or the excess zinc having donor energy level under the conduction band and the UV emission originates from intrinsic excitons in ZnO. The reasons are as follows: (1) High binding energy (59meV) of the exciton in ZnO is an important feature which ensures that the exciton exists at RT. (2) The energy state of exciton is an intrinsic state of the crystal. As a matter of fact, an excitonic state belongs to whole crystal, but in transient time the excitonic states are located in some positions or move from one place to the another in the crystal. So that the better the crystal of ZnO film is, the easier exciton states create. (3) Under high density CR excitation, with the increase of current density ionized hole and electron density and also the exciton density increase, in consequence the UV emission from excitons increases rapidly and the superlinear increase dependence occurs. Relatively speaking, on same condition green emission increases very slowly and a sublinear increase dependence occurs, because the CR excitation energy relatively concentrated from local defect states to exciton states.

If ZnO film has nanometer magnitude structure and it also increase the intensity of oscillator, a strong and resonant coupling between excitons could occur, this is the reason that ZnO thin film may produce direct laser emission.

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## ZnO MSM Ultraviolet Photodetectors

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Recently, there has been an increased interest in high quality ZnO film in order to utilize its optical properties resulting from its direct and wide energy band gap. ZnO is promising for UV photodetector applications due to its wide band gap and large photoresponse. MOCVD is well suited for this purpose as in-situ doped films of high structural quality can be grown economically. In the present study, epitaxial ZnO films were grown on R-plane sapphire substrates using Di-Ethyl Zinc (DEZn) and O<sub>2</sub> in a vertical-flow rotating-disc MOCVD reactor. As DEZn and O<sub>2</sub> react even at room temperature, system modifications were made to minimize gas phase reactions at the growth temperature (350 to 500°C). Beyond 500°C, gas phase reactions were dominant resulting in film degradation and particulate deposition. The orientation relationship between the ZnO films and the R-plane sapphire substrates, and the structural properties were evaluated. The ZnO films showed n-type conductivity under typical growth conditions, which is due to non-stoichiometry (Zn excess). In order to increase the resistivity, nitrogen compensatory doping (from NH<sub>3</sub>) was carried out. The introduction of NH<sub>3</sub> into the growth chamber resulted in film like growth even at temperatures as high as 600°C due to the etching behavior of NH<sub>3</sub>.

A sharp cut-off near 373 nm was observed. The photoresponse drops by more than two orders of magnitude across the cut-off wavelength within 15 nm of the band edge. For a typical MSM photoconductor, both the dark and photo-generated current exhibits a linear relation with bias voltage within 10V, indicating that the devices operates in the photoconductive mode. The low frequency (5 Hz chopping) photoresponsivity in the order of 400A/W at 5V bias was obtained. The minority lifetime of the devices was estimated in the range of 1 μs. This type of photoconductors shows high response speed. The rise time and fall time of 1 μs and 1.5 μs, respectively, were measured using a high-speed pulse laser (pulse duration < 100 fs, frequency = 175 KHz).

It has been reported that the photoresponse of ZnO consists of two parts, a rapid and reproducible solid state process and a slow process with a large response.<sup>[1-4]</sup> The latter is mainly due to a two step process: (i) oxygen adsorption under dark conditions by trapping an electron, then (ii) photodesorption of O<sub>2</sub> by capturing a photo-generated hole. The slow photoresponse is significantly enhanced on the polycrystalline films due to the oxygen adsorption at the ZnO surface and grain boundaries. Fast photoresponse has been achieved in our epitaxial ZnO films based UV detectors in contrast to the polycrystalline ZnO based devices. We believe that the solid state related fast process has been enhanced by the crystalline-quality improvement, which reduces the defects induced recombination. Simultaneously, the O<sub>2</sub> adsorption related slow process has been suppressed by reducing

the electron carrier concentration through N-doping, as well as by essentially eliminating the grain boundaries in the high quality epitaxial ZnO films.

We have also demonstrated ZnO based Schottky photodetectors using Ag as Schottky metals. Both UV illuminated and dark currents show non-linear relation with bias voltage. The photocurrent increases faster with bias than the dark current. At bias of 5V, Schottky photodetector exhibits a dark current of five orders smaller than their photoconductive counterpart.

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## ZnO based lasers: prospects.

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It is now two years since the research groups of Yao [1] and Kawasaki [2] independently reported optically pumped ZnO lasing at room temperature. Whilst not of any great significance to science or device applications (at least not yet) these breakthroughs represent an important milestone in the progress of ZnO epitaxy: epitaxial "optical quality" zinc oxide can now be grown.

These improvements of film properties have implications for those working in photovoltaics, GaN based emission technologies and surface acoustic wave devices. But what are the prospects for ZnO based LED's and laser diodes?

In this presentation we will review the growth techniques that led to the first room temperature lasing demonstrations. In particular we will discuss the growth and optical characterisation of ZnO produced by plasma-assisted molecular beam epitaxy [3].

Directions for future work will be considered, including issues relating to quantum confinement, p-type doping and cavity formation. With reference to work carried out in ZnSe, GaN and CdS based systems.

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## ZnO Powder Lasers

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Traditionally, materials thought to be good for solid state laser applications require a high degree of order. Most solid-state laser materials in production today are grown epitaxially, and therefore require expensive high-vacuum systems and careful lattice matching between film and substrate. This has severely limited the choice of available materials for solid state lasers. In addition, a cavity is essential to a traditional solid state laser since the cavity produces coherent feedback and selects the lasing frequency.

We have recently reported, however, that it is possible to achieve laser action with coherent feedback in highly-disordered, commercial ZnO powder.[1] The powder laser shows a threshold behavior in the integrated emission intensity versus the pump power. The spectral analysis of the emission reveals very narrow (less than 0.3 nm) peaks in the emission spectrum above the threshold. We believe the laser action results from localization of photons within the materials. Essentially, because the powder consists of microcrystals typically less than 100 nm in size, the scattering mean free path is on the order of the wavelength. The recurrent light scattering forms closed loop paths for light. These loops behave as ring cavities for lasers. Therefore, laser cavities are "self-formed" in the highly-disordered media.

In our current work, we attempt to provide a more detailed characterization of the lasing behavior in ZnO powder which we have produced ourselves. The powder is synthesized by a simple method described by Jezequel, *et al.*[2] The powder consists of spherical particles ranging from 0.3 to 3.0  $\mu\text{m}$  in diameter. These particles are comprised of many nanocrystallites, less than 50 nm in size. Heating the powder results in coarsening, an increase in the size of the crystallites, while the larger, spherical particles typically remain separate.

We have demonstrated that ZnO powder produced by this method shows laser action under optical pumping. We seek to determine the relationship between the lasing properties and the structure of the powder. By altering the synthesis conditions we can vary the size of the spherical particles, and by using different annealing conditions we can vary the size of the nanocrystallites to determine what impact these two properties have on the lasing frequencies and threshold. We can also vary the density of particles on a substrate from a film several microns thick, to a sparse dispersion of particles, making it possible to determine whether the lasing arises from inter- or intra-particle scattering.

This work is of particular interest because it demonstrates that laser action can be achieved in ZnO powder which is produced by a simple method using inexpensive equipment and starting materials.

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## P-type layer formation of ZnO by laser doping technique

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### Abstract:

P-type doping was carried out by a laser doping technique for zinc oxide (ZnO) wafer. A procedure of this laser doping process follows. 1) Zinc phosphide ( $\text{Zn}_3\text{P}_2$ ) film as a phosphorous (P) source was deposited on ZnO wafer as 35nm thick. 2) KrF excimer laser radiations were exposed on ZnO wafer with  $\text{Zn}_3\text{P}_2$  film. 3) The  $\text{Zn}_3\text{P}_2$  was decomposed to Zn and P atoms and these atoms diffused into ZnO wafer by excimer laser radiations and its thermal energy. 4) Gold electrodes were evaporated on P doped ZnO wafer. The p-type ZnO layer was formed on ZnO wafer as a result that oxygen atoms in ZnO were replaced to phosphorous atoms.

The  $\text{Zn}_3\text{P}_2$  film was deposited using  $\text{Zn}_3\text{P}_2$  powder (5N of purity) and KrF excimer laser (wavelength: 248nm, a pulse width: 20ns and a pulse energy: 150mJ/cm<sup>2</sup>) were used in this study.

A diode current-voltage (I-V) characteristic was obtained in ZnO pn-diode that was prepared by only laser p-type doping and making electrode because the bulk ZnO wafer that has about 0.2Ωcm of n-type conductivity. The p-type layer formation on ZnO wafer was confirmed by observation of a diode characteristic in this ZnO diode. Moreover, a light emission was observed in this diode at 110 K by current injection as a proof of p-type ZnO layer formation. Figure 1 shows spectra of this light-emitting diode's (LED's) emission at 110K under (a) large current injection (current density: about 30A/cm<sup>2</sup>, bias voltage: 18.4V) and (b) small current injection (current density: about 10A/cm<sup>2</sup>, bias voltage: 10.1V). Fig. 1(C) is photoluminescence spectrum of same sample excited by HeCd laser ( $\lambda=325\text{nm}$ ) at 110K. The light emission was not so strong but it looked like a color of white-violet and which have a peak around 370nm attributed from band edge emission with long wavelength emission of around a 400-600nm region. An inserted picture in figure 1 is a photograph of this ZnO-LED emission under the low current injection at 110K.

Therefore, this laser doping technique has a high potential for ZnO p-type doping. We will report the detail of these results.

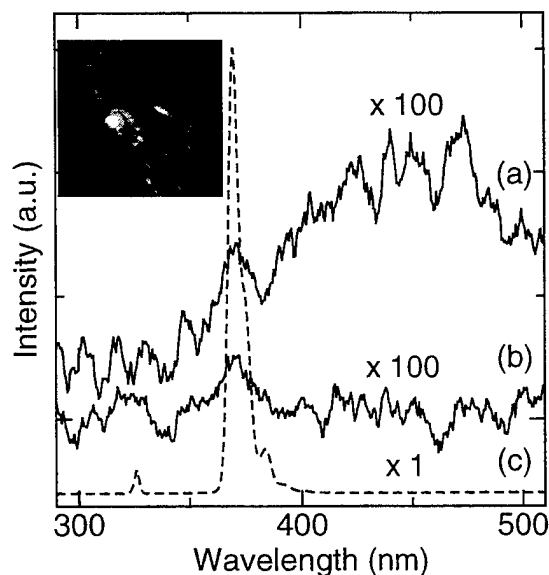


Fig. 1 A spectra of ZnO LED and a photograph of emission at 110K.

## INVESTIGATION OF FUNDAMENTAL EMISSION OF ZnO CRYSTALS GROWN BY RADICAL-BEAM EPITAXY METHOD

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For II-VI wide band compounds the production of exceptionally pure crystals with perfect structure is one of the most important problems. This is connected not only with the fact that reliable fundamental results can be obtained only by taking measurements on a perfect material but also with the fact that the material purity and perfection are of great practical importance.

Exciton photoluminescence (PL) is very sensitive to the quality of crystal structures and to the presence of defects. Therefore, the regularities of the change in exciton spectra as a function of composition and structural peculiarities enable one to use them to control the quality of the crystal optically. Impurities and their associations, main lattice defects and their impurity associations, and exciton and exciton impurity complexes all play an important role in the luminescence, which significantly complicates the observation of free-exciton PL. It is apparent that the more perfect is the crystal, the more probable is the observation of free-exciton PL.

PL spectra of ZnO layers obtained by radical-beam epitaxy (RBE) [1] have been studied.

High-resistivity ZnO layers of  $\approx \mu\text{m}$  thickness obtained by RBE on the basis of ZnO monocrystals with a resistivity  $\rho \approx 10^{11} - 10^{13} \Omega\text{cm}$  were excited by nitrogen laser radiation ( $\lambda = 337.1 \text{ nm}$ ) at liquid-nitrogen temperature  $T = 77 \text{ K}$ . It is remarkable that the complete absence of visible luminescence, intensive bands with  $\lambda_{\text{max}} = 367.7 \text{ nm}$ ,  $\lambda_{\text{max}} = 366.8 \text{ nm}$ , and  $\lambda_{\text{max}} = 362.7 \text{ nm}$  were observed. The half-widths of these bands were, respectively,  $\Delta E = 6 \text{ meV}$  for  $\lambda_{\text{max}} = 362.7 \text{ nm}$  and  $\Delta E = 10 - 12 \text{ meV}$  for the bands  $\lambda_{\text{max}} = 367.7 \text{ nm}$  and  $\lambda_{\text{max}} = 366.8 \text{ nm}$ . After comparison of PL spectrum to reflection spectrum and rely on the Thomas exciton model [2] we can say, that bands in PL spectra are connected with emitting recombination of free A, B and C excitons.

PL spectrum of ZnO layers with a resistivity  $\rho \approx 10^9 - 10^{11} \Omega\text{cm}$  at  $T = 77 \text{ K}$  consist of three peaks:  $\lambda_{\text{max}} = 363.1 \text{ nm}$ ,  $\lambda_{\text{max}} = 366.8 \text{ nm}$  (B exciton),  $\lambda_{\text{max}} = 370.6 \text{ nm}$ . Also in this case the visible part is not observed. The radiation band with a maximum at  $\lambda_{\text{max}} = 363.1 \text{ nm}$  (T band) is reported for the first time, to the best of our knowledge. The band with the maximum  $\lambda_{\text{max}} = 370.6 \text{ nm}$  is known in the literature as M band, and is interpreted in different ways [3 - 5]. The M band appears at low temperatures and at a high excitation level. The characteristic feature of this band is an asymmetric shape and an extended long-wavelength wing. At  $T = 77 \text{ K}$  and a pumping intensity  $I = 10^{14} \text{ W/cm}^2$  in the M-band spectrum, there appears with three maxima:  $M_1$  ( $\lambda = 368.5 \text{ nm}$ ,  $3.362 \text{ eV}$ ),  $M_2$  ( $\lambda = 370.0 \text{ nm}$ ,  $3.348 \text{ eV}$ ),  $M_3$  ( $\lambda = 373.0 \text{ nm}$ ,  $3.322 \text{ eV}$ ). With the pumping intensity increase the M-band structure disappears, and its maximum

is shifted toward the long-wavelength side of the spectrum. The obtained experimental spectra can be explained by the presence of the following three channels of exciton molecule (EM) decay.

(1) As a result of the EM decay a lightlike state  $M_1$  of the lower polariton branch (LPB) and an excitonlike state of the LPB are formed. On reaching the crystal surface the lightlike polariton escapes as a luminescence photon  $M_1$  ( $\lambda=368.5$  nm, 3.362 eV).

(2) The EM causes a lightlike state of the LPB and a longitudinal exciton state  $B_L$ . Reaching the crystal surface the lightlike polariton escapes as a photon  $M_2$  ( $\lambda=370.0$  nm, 3.348 eV).

(3) The EM decay results in the appearance of two lightlike polaritons of the lower and upper (UPB) branches. Both polaritons reach the crystal surface and escape as photons  $M_3$  ( $\lambda=373.0$  nm, 3.322 eV) and T ( $\lambda=363.1$  nm, 3.412 eV).

Thus the T band is ascribed to radiation of a polariton of the upper branch. The exciton molecule energy in ZnO is within  $6.7310 < E_{EM} < 6.740$  eV, which corresponds to the interval  $362.49 \leq \lambda_{UPB} \leq 363.49$  nm for the wavelength of radiation from the upper polariton branch. The obtained  $\lambda_{UPB}$  value is in perfect agreement with the T-band position (363.1 nm).

The presence of free-exciton radiation bands in photoluminescence spectra and the absence of visible luminescence suggest that the ZnO films, obtained by RBE, are characterized by a high structural perfection up to the thin near-surface region and a negligible content of uncontrollable defects and impurities.

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## OPTICAL AND ELECTRICAL PROPERTIES OF n- AND p-TYPE ZnO LAYERS

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Production and investigation of  $A_2B_6$  wide-band gap semiconductor compounds is one of the most actual problems of optoelectronics. But their use is very limited due to the difficulties, connected with regulation of their electrical and optical properties. Especially this concerns with ZnO compound. To solve the problem of conductivity type inversion in this compound, it was necessary to determine the range of temperature and pressure of non-metal component vapor, on the base of thermodynamical analysis. Under these conditions of heat-treatment in non-metal component vapor atmosphere, it is possible to obtain p-type conductivity. We proposed the new method (Radical Beam Epitaxy). In our method all features of oxygen, due to which oxygen is chemically comparatively less active, were taken into account.

This method enables one to obtain monocrystalline ZnO layers on the base of Zn - VI non-metal compounds. In RBE method base crystals are treated in the atmosphere of singlet oxygen radicals. This atmosphere is created by rf discharge. The rf oscillator converts the molecular oxygen stream into plasma, which contains in addition to singlet oxygen radicals, oxygen ions, triplet oxygen radicals and electrons. An applied magnetic field causes "filtration" after which only singlet oxygen radicals reach the base crystal. Due to its activity such oxygen interacts with the base crystal and form new ZnO monocrystalline layers.

The distance  $d$  between the plasma and the base crystal is controlled by the magnetic field. The experiment shows that the optimal distance  $d$  between plasma and the base crystal is controlled by the magnetic field. The experiment shows that the optimal distance  $d \approx 2.5 \text{ cm}$ . At  $d < 2.5 \text{ cm}$  crystal evaporation (ion etching) takes place; at  $d > 2.5 \text{ cm}$  there is a sharp decrease in the atomic oxygen stream falling into the crystal surface, which reduces the layer growth efficiency.

From the aforesaid it might be assumed that RBE differs from classical epitaxy in that one component (oxygen) comes from the gaseous phase and the second component (metal) - from the crystal bulk. The second important peculiarity of RBE is the temperature distribution in the reactor. The base crystal is in the high-temperature narrow zone of the reactor. In other parts the temperature is much lower. Such distribution profile removes uncontrollable impurities from the film growth zone, since they move to the low-temperature parts of the reactor. The base crystal temperature can be within  $150^\circ\text{C} \div 950^\circ\text{C}$ . The radical concentration is  $1 \cdot 10^{14} \div 5 \cdot 10^{15} \text{ cm}^{-3}$ . In the case of thermal dissociation at  $T = 1000 \text{ K}$  this concentration of radicals can be obtained only when the molecular oxygen pressure is  $P_{O_2} = 10^6 \text{ atm}$ . In our case the total pressure was  $0.1 \text{ atm}$ , i. e. in the reactor the "effective pressure" from the viewpoint of singlet oxygen radical concentration is nearly  $10^7$  times higher than the actual pressure. Using the RBE method epitaxial layers with thickness from some atomic layers up to  $50 \mu\text{m}$  can be obtained.

It has been proved experimentally that the inversion of conductivity occurs below  $650^{\circ}\text{C}$  under given circumstances. The visible part is completely absent in PL spectra at the growth temperature  $T=650^{\circ}\text{C}$ . The resistivity of these samples was  $\rho > 10^{13} \text{ ohm cm}$ . Subsequent lowering of the growth temperature leads to the increase of the intrinsic defect hole conductivity of samples with pronounced hole conductivity grown at the temperature  $350^{\circ}\text{C}$  ( $\rho=10^2 \text{ ohm cm}$ ;  $\mu_p=23 \text{ cm}^2/\text{Vs}$ ;  $N_p=4 \times 10^{14} \text{ cm}^{-3}$ ).

After removing of new grown layers, the layers of base crystal, near the surface, have hole conductivity. P-type conductivity is caused by the increasing of concentration of metal vacancies. During the fixed value of non-metal radical concentration and by various temperatures, the concentration of metal vacancies is changed. This fact gives possibility to regulate stoichiometry of the crystal.

So, it was obtained high pure monocrystalline ZnO layers [1] with hole conductivity, electron conductivity and dielectrics.

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